Inelastic scattering at the 3d- and 4d-4f thresholds of Lanthanides

A. Moewes[1], D.L. Ederer[2], E.Z.Kurmaev[3], M.M. Grush[4], and T.A. Callcott[4]

[1] *Center for Advanced Microstructures and Devices, CAMD at Louisiana State University, Baton Rouge, LA 70803*

[2] *Department of Physics, Tulane University, New Orleans,LA 70118, USA*

[3] *Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg GSP-170, Russia*

[4] *University of Tennessee, Department of Physics, Knoxville, TN 37996*

We have used soft x-ray inelastic scattering based on excitation with monochromatic synchrotron radiation to elucidate the role of 4f electrons in recombination processes at the 3d-4f and 4d-4f thresholds of Nd_2O_3 [1] and $LaAlO_3$ [2]. The experiments are performed at the undulator beamline 8.0.1 of the Advanced Light Source utilizing the spherical grating monochromator and the Rowland circle endstation.

1. Nd_2O_3

At excitation energies above the M_{IV} ($3d_{3/2}$) threshold, we observe Coster-Kronig ($3d_{3/2} \rightarrow 3d_{5/2}$) enhanced fluorescence from the refill of the M_V ($3d_{5/2}$) hole via the 5p and 4f channel. Fluorescence occurs mainly due to transitions in which charge-transfer provides additional 4f electrons. Resonant inelastic scattering dominates the emission process and we observe two energy loss features at 21 and 2.3 eV, which are due to net transitions 5p to 4f ($5p^6 4f^3 \rightarrow 5p^5 4f^4$) and 4f-inner shell excitations [3] $4f^3 \rightarrow (4f^3)^*$ respectively.

When comparing the emission spectra excited through the 3d-4f and the 4d-4f threshold, we note some aspects that are different:

- The contribution of non-dipole transitions ($^4I \rightarrow {}^2G$, ^2H) to the inelastic scattering is stronger at the 3d than at the 4d threshold.
- Only the 3d-4f spectra exhibit charge-transfer and Coster-Kronig processes.
- While the main inelastic process at both thresholds is the excitation of the electrons within the 4f shell (2.3 eV energy loss), the 5p-4f energy loss (21 eV) is not apparent at the 4d threshold.
- At the 4d threshold, radiationless processes such as Auger-electron emission and autoionization suppress fluorescence from the decay of the vacancy in the d-shell via the 4f channel.

Our calculations of the emission spectra make use of the Kramers-Heisenberg formula and are in excellent agreement with the experimental results emphasizing the localized character of the 4f electrons.

2. $LaAlO_3$

At excitation energies above the M_{IV} edge of La we also observe Coster-Kronig enhanced fluorescence that refills the 3d hole via 5p and 4f electrons. We find a new delayed onset of the fluorescence as the 7.5 eV inelastic scattering evolves into 3d-4f emission about 8 eV above the absorption threshold which we attribute to the energy required to produce a charge-transfer hole. Raman scattering with a net energy loss between the initial and the final states of 7.5 and 16.3 eV is observed. We suggest that the 7.5 eV inelastic scattering feature whose excitation energy is about 8 eV higher than the 3d-4f absorption feature arises from a 4f $\underline{L}$ charge-transfer. According to our calculations, the 16.3 eV loss is due to the promotion of a 5p electron into a 4f orbit. Due to the high degree of localization of the 4f electrons, calculations based on a purely atomic model provide a consistent interpretation of the observations. One of the surprising outcomes of these measurements has been the observation that inelastic scattering provides the major contribution to the x-ray emission between the M_V and the M_{IV} absorption thresholds. This is due to the fact that the M shell fluorescence yield is of the order of 0.5%. Secondly it is surprising to see how C-K transitions “switch on” fluorescence once the threshold energy has been achieved.

This work was supported by National Science Foundation grant DMR-9017997, the Science Alliance Center for Excellence Grant from the University of Tennessee and a DoE-EPSCor cluster research grant DoE-LEQSF (1993-95)-03. The Advanced Light Source is supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under contract no. DE-AC03-76SF00098.

[1] A. Moewes, D.L. Ederer, M.M. Grush and T.A. Callcott, Phys. Rev. B 59, 5452 (1999).
[2] A. Moewes, S. Stadler, R.P. Winarski, M.M. Grush, T.A. Calcott, and D.L. Ederer, Phys. Rev. B 58, Rap. Comm. R15951 (1998).
[3] A. Moewes, T. Eskildsen, D.L. Ederer, J. Wang, J.Mc. Guire, and T.A. Callcott, Phys. Rev. B 57, Rap. Comm. R8059 (1998).

Principal investigator: Alexander Moewes, Center for Advanced Microstructures and Devices, Louisiana State University. Email: moewes@lsu.edu. Telephone: (225) 388-0419.